Journal of the Ceramic Society of Japan, Supplement 112-1, PacRim5 Special Issue, 112 [5] S591-S594 (2004)

Paper

Quick Fabrication of Highly Oriented Bi-2223 Superconducting Ceramics Using Plate-Like Seed Crystals

Hidenobu ITOH, Koji TAKEDA, Masami KISHI* and Junichi TAKAHASHI**

Kitami Institute of Technology, 165, Koen-cho, Kitami 090-8507, Japan

*Division of General Education, Hokkaido Institute of Technology, 7-15, Maeda, Teine-ku, Sapporo 006-8585, Japan

**Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, West 8, North 13, Kita-ku, Sapporo 060-8628, Japan

We have successfully prepared plate-like fine powder of high-Tc phase (2223) superconducting oxide with preferential 002 faces by grinding in dehydrated pure ethanol. In the current study, we attempted quick fabrication of highly oriented (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ superconductor using plate-like seed crystals. It was found that the addition of the seed to the commercial precursor (Dowa Kogyo) brought about a considerable reduction in fabrication time. Almost all single phase (2223) sintered superconducting oxide was obtained by heating the precursor mixed with 30 wt% seed for 4 h at 870°C. Furthermore, the grains of the sintered disk were highly oriented.

[Received July 25, 2003; Accepted December 24, 2003]

Key-words : *Superconductor, Bi-Pb-Sr-Ca-Cu-O system, 2223 phase, Seed crystal, Quick fabrication, Grain-orientation*

1. Introduction

Since the discovery of Bi-based high-Tc superconductors,[1] much effort has been focused on the development and commercialization of this new material. Bulk ceramic superconductor is a candidate for potential applications (i.e., superconducting magnetic energy storage systems, fault-current limiters, and magnetic resonance imaging systems require current lead with a high current capacity and low thermal conductivity,[2] although it is very difficult to prepare dense superconducting oxide. It has been reported that during sintering, "a retrograde densification" occurs, resulting in a reduction of density prior to final densification.[3] The retrograde densification mechanism has been shown to be that of the formation of thin plate-like crystallites, which grow in a randomly oriented fashion, thus pushing the structure apart. Therefore, inducing grain orientation and short-term sintering (quick fabrication) would be effective for fabrication of dense superconducting oxide.

J. A. Horn *et al.*[4] prepared highly textured bismuth titanate (BiT) by templated grain growth using platelet-shaped particles of BiT. The same idea might be applied to the Bi-based high-Tc ceramic superconductor. It is expected that the addition of platelet-shaped seeds to the precursor would be efficacious not only for "quick fabrication," but also for grain orientation improvement. We have successfully prepared plate-like fine powder of 2223 phase superconducting oxide with preferential 002 faces by grinding in dehydrated pure ethanol.[5] In the current study, we attempted quick fabrication of highly oriented (Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ superconductor using plate-like seed crystals.

2. Experimental Procedure

The fine seed crystals were prepared as follows: Powder with a nominal composition of Bi$_{1.6}$Pb$_{0.4}$Sr$_{2.0}$Ca$_{2.0}$Cu$_{3.0}$O$_x$ was prepared using an improved co-precipitation method;[5] mixed metal oxalates were precipitated from homogeneous acetic acid solution by adding dimethyl oxalate and calcined at 500°C for 5 h. The calcined powder was pelletized (20 mm in dia. 0.51×10^3 kg/cm^2) and sintered at 855°C for 24 h. Then the pellets were ground in dehydrated ethanol using a planetary micro mill (Fritsch P-7) with a 45 ml bottle and agate balls for 10 min to form fine plate-like 2223 phase superconducting oxide particles.[6]

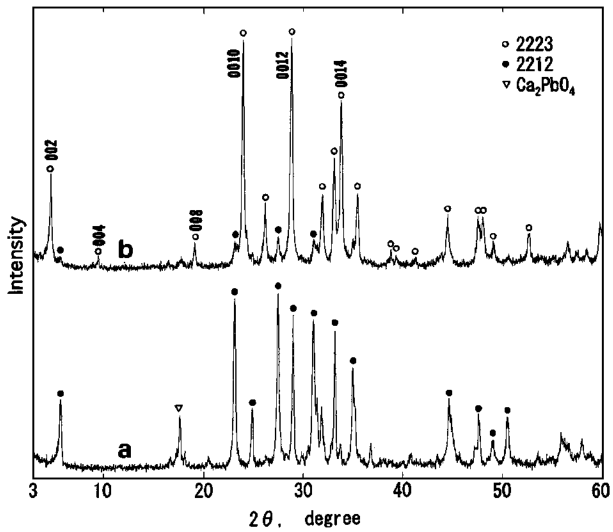

Fig. 1. XRD patterns of the commercial precursor (a) and the seed powder (b)

The grounded seed crystals were added to the commercial precursor (Dowa Kogyo), whose composition was Bi$_{1.85}$Pb$_{0.35}$Sr$_{1.90}$Ca$_{2.05}$Cu$_{3.05}$O$_x$, and structure is mainly low-Tc 2212 phase (see **Fig. 1**) with median particle size of 2.12 μm, then mixed in dehydrated ethanol using a ball mill for 10 min. After drying at 120°C for 12 h, the mixture was pressed to a disk (10 mm in dia. 2.5×10^3 kg/cm^2) and fired at various temperatures in atmospheric conditions. The resultant phases were determined using an X-ray powder diffractometer with CuKα radiation in the 2θ range from 3 to 60 degrees. Differential thermal analysis (DTA) was employed to investigate the reaction mechanism with heating rate of 5°C/min for 20 mg of the sample.

3. Results and discussion

3.1 Crystalline structure and shape of the seed crystals

Figure 1 shows the X-ray diffraction (XRD) patterns of the

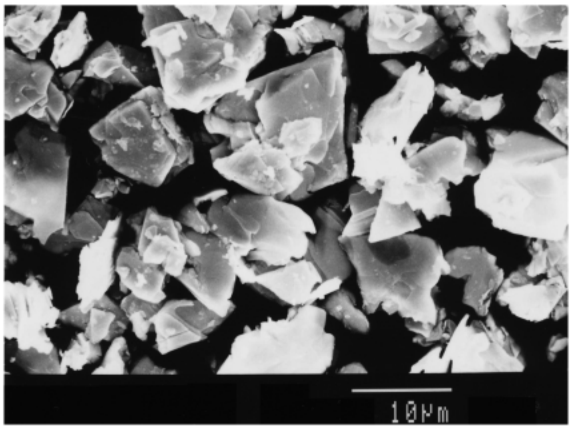

Fig. 2. SEM photograph of the seed powder

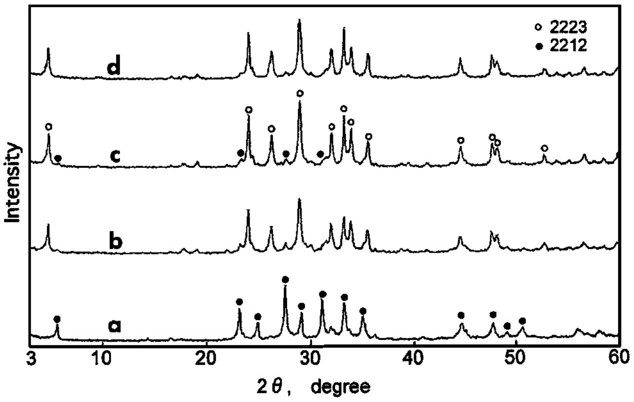

Fig. 3. XRD patterns of the samples with various amounts of the seed fired at 870°C for 4 h
a: 0 wt%, b: 10 wt%, c: 20 wt%, d: 30 wt%

seed powder milled in dehydrated pure ethanol. Some weak diffraction peaks due to low-Tc phase (2212) appeared, although the main crystalline structure was determined as high-Tc phase (2223). After milling, the diffraction peak height assigned to 00n planes increased considerably.[6] A SEM photograph of the seed crystals is shown in **Fig. 2**. The particles appeared to be plate-like. The average particle size was 4.4 μm as analyzed using a Shimadzu SLAD–2100 Particle Size Analyzer.

3.2 Effect of seed on formation of 2223 phase from commercial calcined precursor

Figure 3 shows XRD patterns of the sintered disks with various amounts of seed fired for 4 h at 870°C. For the commercial calcined precursor after being fired at 870°C for 4 h (a), almost all the peaks observed were peaks due to the low-Tc phase. However, for seeded precursors (b–d), the peak intensities of the low-Tc phase decreased and conversely, that of the high-Tc phase grew drastically. In the pattern for the sample with 30 wt% of seed (d), almost all the peaks can be assigned to the high-Tc phase. These results clearly demonstrate that the addition of seeds to the calcined precursor facilitate the formation of high-Tc phase. **Figure 4** shows the XRD patterns for the samples with 10 wt% seed after being fired at 860–880°C for 6 h. When the sample was fired at 860°C, the XRD peaks assigned to low-Tc phase remain in large quantities, indicating that the temperature is insufficient to form

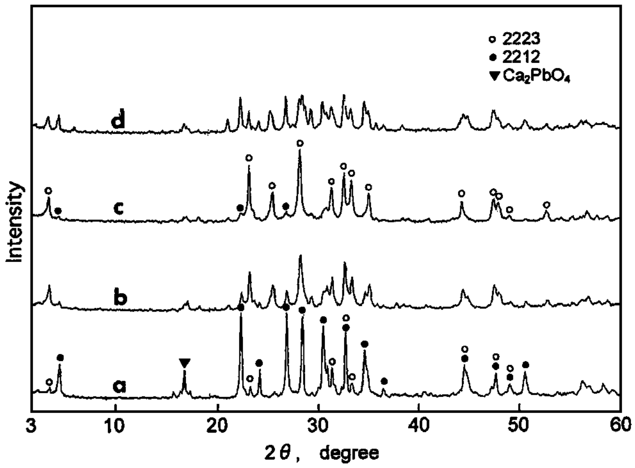

Fig. 4. XRD patterns of the samples with 10 wt% of the seed fired at various temperatures for 6 h
a: before firing, b: 860°C, c: 870°C, d: 880°C

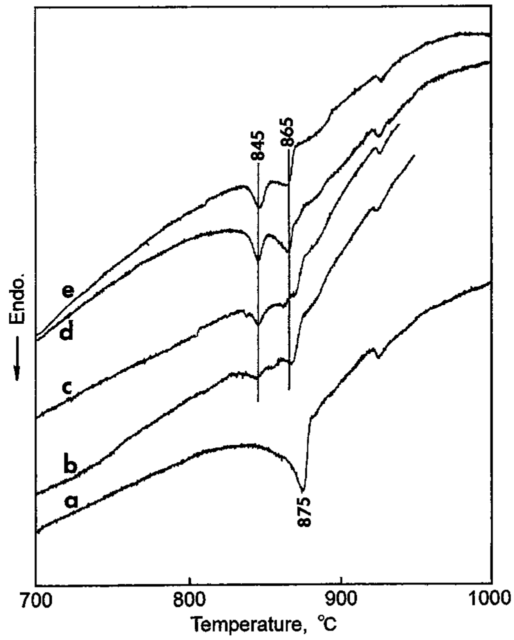

Fig. 5. DTA curves of the samples with various amount of seed
a: 100 wt% (seed), b: 50 wt%, c: 30 wt%, d: 10 wt%, e: 0 wt% (precursor)

high-Tc phase. Conversely, firing at temperatures higher than 880°C caused partial melting of the sample disks and an increase in low-Tc phase compared with those fired at 860°C. In conclusion, the optimum temperature for the formation of the high-Tc phase from the seeded precursor is found to be 870°C.

Figure 5 shows the DTA curves of the calcined precursors mixed with various amounts of seed. It is well known that the DTA curve of calcined precursor has two endothermic peaks in the temperature range of 840°C to 880°C. Hatano *et al.*[7] suggest that the peak observed at a low temperature (845°C) is closely connected with the partial melting. The partial melting is considered as a very important step for high-Tc phase formation, because the partially melted liquid phase offers a fast diffusion path for the elements required to form the high-Tc

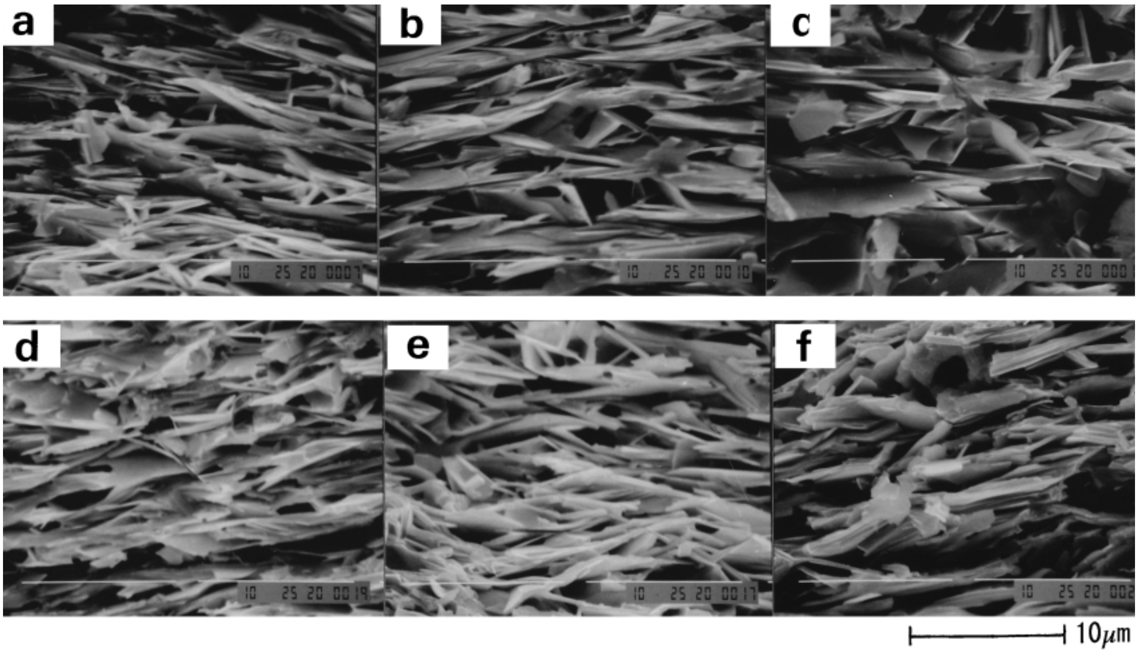

Fig. 6. SEM photographs of the sintered disks fired at 870°C for 2 h (a, d), 6 h (b, e), and 12 h (c, f): 10 wt% (a, b, c) or 50 wt% (d, e, f) of seed were added

phase.[7] The endothermic peak temperature at 845°C did not change with the amount of seed, suggesting that the seed does not act to produce another new intermediate. The decrease in peak intensity with the increase in the amount of seed may be due to the amount of precursor.

On the other hand, the endothermic peak observed at a relatively high temperature (865°C) represents the melting of the low-Tc phase. Hatano *et al.*[7] and Kijima *et al.*[8] reported that the high-Tc phase is produced through the low-Tc phase, which was formed as an intermediate reaction product and also as a precursor of the High-Tc phase. Therefore, high-Tc phase should actually be formed in the temperature range of 845°C to 865°C. It should be noted that the temperature range of 845°C to 865°C is a little lower than the temperature at which the seeds melt (5–a). At the optimum temperature for formation of high-Tc phase (870°C), the molten precursors (low-Tc phase and the others) react to form high-Tc phase on the seed, which does not melt at that temperature, and grows the seed crystals.

3.3 Density and grain orientation of the sintered disk

Figure 6 shows SEM photographs of the fractured surface of the sintered disks parallel to the pressing axis. It is clear that the degree of the grain orientation of sintered disks improved with the increase in the amount of added seed. The plate-like seed crystals added to calcined precursor were oriented during the pressing process, and was followed by crystal growth by heating at 870°C in the mechanism described above. The figure also shows that long-term firing (12 h) causes "retrograde densification."

The geometrical density of the fired disks with various amount of seed crystals is shown in **Fig. 7**. The density increased with an increase in the amount of seeds, although contrary to expectations, the relative density was not so high. To some extent, addition of seeds to calcined precursor, but may not effect the densification of high-Tc phase superconductor compared with those prepared by the hot pressing technique (HP).[9] The technique involving combining HP with seeds described in this paper, would be effective for quick fabrication of dense high-Tc superconducting ceramics.

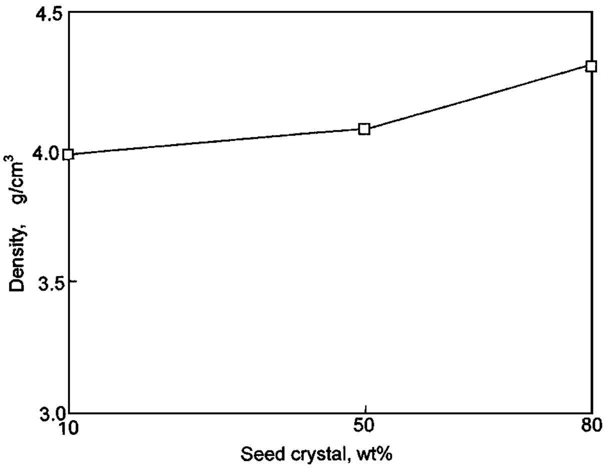

Fig. 7. Geometrical density of the sintered disks with various amounts of seed fired at 870°C for 6 h

4. Conclusions

Plate-like seed crystals were added to commercial calcined precursor, and the effects of the seeds on formation of high-Tc phase (2223) were investigated. The results were summarized as follows:

1. The rate of formation of high-Tc phase from commercial calcined precursor was greatly accelerated by adding seed crystals. It was found that almost all high-Tc phase sintered superconducting oxide was obtained by heating the precursor mixed with 30 wt% seed for 4 h at 870°C.
2. The optimum firing temperature for the seeded precursor was 870°C. At the optimum temperature, the molten precursors (low-Tc phase (2212) and the others) react to form the high-Tc phase on the seed crystals, which does not melt at that temperature, and grows the seed crystals.

3. The plate-like seed crystals in the calcined precursor were easily oriented during the pressing process and were followed by a crystal growth by heating at 870°C

Acknowledgement The authors are grateful to Mr. J. Kokado for his support during the experiment.

References

1) Maeda, M., Tanaka, T., Fukutomi, M. and Asano, T., *Jpn. J. Appl. Phys.*, Vol. 27, pp. L209–L210 (1988).
2) Thayer, R. L., Schmidt, S. R., Dorris, S. E., Bullard, J. W. and Lanagan, M. T., *J. Am. Ceram. Soc.*, Vol. 83, pp. 2365–2368 (2000).
3) Johnson, Jr. D. W. and Rhodes, W. W., *J. Am. Ceram. Soc.*, Vol. 72, pp. 2346–2350 (1989).
4) Horn, J. A., Zhang, S. C., Selvaraj, U., Messing, G. L. and Trolier-McKinstry, S., *J. Am. Ceram. Soc.*, Vol. 82, pp. 921–926 (1999).
5) Itoh, H., Okada, K., Fujisawa, T., Okazaki, N. and Tada, A., *Chem. Lett.*, pp. 429–432 (1990).
6) Itoh, H., Nakai, K., Motai, S. and Maeda, S., *J. Mater. Synthesis & Processing*, Vol. 7, pp. 145–150 (1999).
7) Hatano, T., Aota, K., Ikeda, S., Nakamura, K. and Ogawa, K., *Jpn. J. Appl. Phys.*, pp. L2055–L2058 (1988).
8) Kijima, N., Endo, H., Tsuchiya, J., Sumiyama, A., Mizuno, M. and Oguri, Y., *Jpn. J. Appl. Phys.*, pp. L1852–L1855 (1988).
9) Murayama, N., Sudo, E., Awano, M., Kani, K. and Torii, Y., *Jpn. J. Appl. Phys.*, pp. L1856–L1858 (1988).